

ORGANO-METALLIC INTERACTIONS IN SOILS: 2. REACTIONS BETWEEN DIFFERENT FORMS OF IRON AND ALUMINUM AND THE ORGANIC MATTER OF A PODZOL BH HORIZON

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In a previous paper (9) reactions between the organic matter (O.M.) of a podzol B_h horizon and a number of metal ions were described. The formation of a range of iron- and aluminum-O.M. complexes, varying from 1 to 6 moles of metal per mole of O.M. and becoming increasingly water-insoluble as more metal was complexed, was indicated in those experiments.

In podzol profiles the most abundant inorganic constituents, aside from silicon, are aluminum and iron. The pH in the upper horizons of such soils ranges between approximately 4 and 5. Under these conditions the O.M. would be expected to react primarily with hydroxylated forms of iron. In the case of aluminum, because of greater solubility, considerable quantities of Al⁺⁺⁺ ions in addition to partially hydroxylated compounds, should be available for reaction with O.M.

Knowledge (8) that the molecular weight of this O.M. was 670 and its molecular formula C₂₁H₁₂(COOH)₈(OH)₅(CO)₂, was of valuable assistance in interpreting the results. It made it possible to express metal uptake data in terms of molar in addition to weight ratios.

The purpose of the present paper is threefold: (a) to determine, in terms of molar as well as weight ratios, amounts of iron and aluminum taken up by O.M. from various metal sources, such as hydrous oxides, exchangeable forms, and from a soil material containing appreciable amounts of "free iron" and easily soluble aluminum; (b) to compare these data with results obtained in the earlier research (9) and (c) to obtain additional information on the role of functional groups in these organo-metallic reactions.

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MATERIALS AND METHODS

O.M. was extracted from a sample of the B_h horizon of the Armadale profile, a podzol developed on sandy loam. Methods of extraction, purification, and concentration of O.M. were analogous to those described previously (9). A stock solution of O.M., containing 3.8 mg./ml. was prepared.

The same soil sample was used in the uptake experiments [procedures *F*(1) and *F*(2)].

Analytical grade Amberlite IR-120 exchange resin, 8 to 10 per cent divinylbenzene and containing 44 to 48 per cent moisture, was employed. For the preparation of metal-enriched resins, portions of the latter were leached with a large excess of slightly acidified *N* FeCl₃ and AlCl₃ solutions, respectively. The resins were then washed thoroughly with distilled water until the test for chloride was negative and the pH of the effluent solutions was equal to that of distilled water.

Samples of goethite and gibbsite were purchased from Ward's Natural Science Establishment, Inc., Rochester, N. Y.

Iron and aluminum uptake

Three sources for both iron and aluminum were used. For iron these were goethite, iron-saturated resin, and soil. For aluminum they were gibbsite, aluminum-saturated exchange resin, and the soil. The soil sample contained 1.88 per cent total Fe₂O₃, 0.91 per cent "free" Fe₂O₃, 8.31 per cent total Al₂O₃ and 1.06 per cent easily soluble Al₂O₃ (6, 7).

In all experiments metals were supplied in considerable excess over what was taken up by O.M.

The effects of pH, standing and shaking, intermittent and continuous leaching, and of atmosphere (air *vs.* nitrogen) on metal uptake by O.M. were also investigated.

The experimental details were as follows:

Procedure A: 25-ml. aliquots of O.M. solution (= 95.0 mg. of O.M.) were pipetted into a series of 50-ml. glass-stoppered Erlenmeyer flasks, containing 45 mg. of goethite or gibbsite, respectively. The suspensions were adjusted to pH 3, 5, and 7 with the aid of a pH meter. One set of suspensions was allowed to stand in the laboratory [A(1)] while another set was shaken continuously [A (3)]. In the case of iron, separate sets of suspensions were maintained under air and under nitrogen [A(2) and A(4)]. The period of contact was 1 week in each case; after this, the suspensions were centrifuged at 2000 rpm for 15 minutes. The supernatant solutions were then decanted, evaporated to dryness on the steam bath, and digested with small portions of 5:1 $\text{HNO}_3\text{-HCl}$ until all organic matter was destroyed. The inorganic residue was made up to a fixed volume with distilled water, and aliquots were analyzed for iron using o-phenanthroline (10) and aluminum employing aluminon (5).

Procedure B: Mixtures of 4.5 g. of purified sand and 45 mg. of either goethite or gibbsite, supported by plugs of glass wool in 25-ml. burettes, were leached with separate 25-ml. aliquots of O.M. solution adjusted to pH 3, 5, and 7. The columns were kept wet during working hours and left undisturbed overnight. The experiments lasted 1 week, after which the suspensions were centrifuged, evaporated to dryness, and processed as under procedure A.

Procedure C: Mixtures of 4.5 g. of purified sand and 45 mg. of goethite, placed in separate sets of perfusion apparatuses of the type described by Audus (1), were leached continuously for 1 week with 25 ml. of O.M. solution adjusted to pH 3, 5, and 7. The leachates were then evaporated to dryness and analyzed for iron, following digestion, as outlined under procedure A.

Procedure D: Separate 5-g portions of iron-saturated and of aluminum-saturated exchange resin (holding 234 mg. of Fe^{+++} and 120 mg. of Al^{+++} respectively), supported by plugs of glass wool in 25-ml. burettes, were leached for 1 week with 25-ml. aliquots of O.M. solution adjusted to pH 3, 5, and 7. The resins were leached during working hours and allowed to dry overnight. Analyses for iron and aluminum, following digestion, were performed as described under procedure A.

Procedure E: Separate 5-g portions of iron-saturated and of aluminum-saturated exchange resin, placed on top of 4.5 g. of purified sand in a perfusion apparatus, were leached for 1 week with 25 ml. of O.M. solution adjusted to pH 5.0 prior to leaching. Following centrifugation, the supernatant solutions were evaporated to dryness, digested, and analyzed for iron and aluminum, respectively, as described under procedure A.

Procedure F: 1-g. portions of soil in 50-ml. ground-glass stoppered Erlenmeyer flasks were shaken continuously for 1 week with 25 ml. of O.M. solution. Separate sets of suspensions were adjusted to pH 3, 5, and 7 prior to shaking. One set of suspensions was shaken under air [F (1)], another under nitrogen [F (2)]. Following centrifugation, the supernatant solutions were processed as described under procedure A.

All results were corrected for iron and aluminum present in the original organic matter.

Methylation of O.M.

One g. of O.M., dissolved in 40 ml. of methanol in a 125-ml. Erlenmeyer flask, was cooled in an icebath. Diazomethane in ether, generated from 20.6 g. of nitrosomethyl urea, was distilled into the alcoholic solution (11). After allowing the suspension to stand in contact with diazomethane for 24 hours in the refrigerator, the excess diazomethane was evaporated with gentle heating and the methylated product dried under reduced pressure at room temperature. Methoxyl analysis (2) of the methylated O.M. showed 14.2 per cent OCH_3 as compared with 0.6 per cent OCH_3 for the untreated O.M. The increase in the methoxyl content was thus 13.6 per cent, corresponding to the methylation of approximately three equivalents of acid groups per molecular weight.

Another 1-g. sample of O.M. was methylated twice by the procedure outlined above. The increase in methoxyl content for this sample was 24.8 per cent, corresponding to the methylation of approximately six equivalents of acid groups per molecular weight.

The two methylated samples are referred to as Methylated O.M.-I and Methylated O.M.-II.

Both materials were no longer water-soluble, but were soluble in methanol. Iron uptake was measured by shaking 100 mg. of untreated O.M. and of each of the methylated fractions, sus-

pended in 25 ml. of 80 per cent aqueous methanol, with 5 g. of iron-saturated Amberlite IR-120 exchange resin for 2 hours. Separate sets were adjusted to pH 3 and 5. Following filtration, aliquots of the clear filtrate were evaporated, digested with $\text{HNO}_3\text{-HCl}$, and analyzed for iron as under procedure A.

RESULTS

The uptake of iron and aluminum from goethite and gibbsite, respectively, is shown in table 1. More iron was taken up on shaking than on standing, regardless of whether this was done under air or nitrogen [procedures A (1) and A (4)]. There was little difference in iron taken up on standing under air *vs.* standing under nitrogen, and on shaking under air *vs.* shaking under nitrogen. Iron uptake decreased with rise in pH. In the case of aluminum, uptake decreased even more significantly with rise in pH. It made little difference whether the suspensions were allowed to stand or to shake. In terms of mmoles of metal per mole of O.M., more Al and Fe was taken up at pH 3, but considerably less at pH 5 and 7. The final pH rose in all instances.

On intermittent leaching (table 1, procedure B) less iron was abstracted from goethite than on standing or shaking, although considerably more aluminum was mobilized under these conditions. Again there was a decrease in metal uptake with rise in pH, especially in the case of iron. The final pH values also rose.

Continuous leaching in a perfusion apparatus (table 1, procedure C) offered the most favorable conditions for the uptake of iron from goethite. Regardless of pH, approximately 1 mole of iron per mole of O.M. was mobilized. The final pH of the system originally adjusted to pH 5 dropped to pH 3.3.

On intermittent leaching, more iron and aluminum (except at pH 3) was taken up from iron- and aluminum-saturated exchange resin (table 2, procedure D) than from goethite and gibbsite, respectively, under similar conditions. Maximum amounts of iron were removed at pH 5. The amounts of aluminum taken up, however, increased with rise in pH. The final pH values of the suspensions originally adjusted to pH 5 and 7 dropped for both metals, whereas the pH of the solutions originally adjusted to 3 rose slightly.

The data for procedure E are most interesting. By continuous leaching in a perfusion apparatus

TABLE 1
Iron and aluminum uptake from goethite and gibbsite

Procedure	Goethite			Gibbsite		
	mg. Fe/g. O.M.	mmoles Fe/mole O.M.	Final pH	mg. Al/g. O.M.	mmoles Al/mole O.M.	Final pH
A (1)						
pH 3	6.8	81.6	3.3	6.0	149.4	3.3
pH 5	5.6	67.7	5.6	1.3	33.2	5.4
pH 7	5.0	59.5	7.6	0.3	8.2	7.5
A (2)						
pH 3	6.9	83.2	3.3			
pH 5	4.6	55.4	5.6			
pH 7	4.7	56.3	7.5			
A (3)						
pH 3	9.5	114.2	3.3	5.2	129.5	3.3
pH 5	7.5	89.8	5.6	1.1	26.7	5.3
pH 7	6.2	74.2	7.6	1.1	26.7	7.2
A (4)						
pH 3	11.9	143.0	3.5			
pH 5	7.3	87.3	5.6			
pH 7	5.9	70.9	7.6			
B						
pH 3	4.6	55.4	3.7	23.0	574.4	3.5
pH 5	3.5	42.4	5.8	22.5	561.4	5.4
pH 7	1.7	20.6	7.6	18.8	468.4	7.2
C						
pH 3	87.3	1,048.9	3.3			
pH 5	90.7	1,089.8	3.3			
pH 7	90.7	1,089.8				

A (1) = Standing under air (goethite and gibbsite).

A (2) = Standing under nitrogen (goethite).

A (3) = Shaking under air (goethite and gibbsite).

A (4) = Shaking under nitrogen (goethite).

B = Intermittent leaching (goethite and gibbsite).

C = Perfusion (goethite).

approximately 1.0 mole of ferric iron and 1.1 mole of aluminum were taken up from iron- and aluminum-saturated exchange resins, respectively. Again the final pH values were lower than those of the original solutions.

Shaking under air *vs.* shaking under nitrogen had little effect on the amounts of iron, and

TABLE 2
Iron and aluminum uptake from metal-enriched
exchange resins and from soil

Method	Iron			Aluminum		
	mg. Fe/g. O.M.	mmoles Fe/mole O.M.	Final pH	mg. Al/g. O.M.	mmoles Al/mole O.M.	Final pH
<i>D</i>						
pH 3	8.0	96.3	3.3	18.0	448.7	3.1
pH 5	31.3	375.5	3.2	28.7	714.9	3.8
pH 7	4.4	53.1	3.4	31.7	791.2	4.2
<i>E</i>						
pH 5	85.9	1,032.2	3.2	44.2	1,102.9	3.9
<i>F(1)</i>						
pH 3	6.1	73.5	4.0	19.2	479.2	4.0
pH 5	10.5	126.5	5.5	26.5	660.0	5.5
pH 7	9.5	114.3	6.0	22.9	570.2	6.0
<i>F(2)</i>						
pH 3	6.3	75.9	4.1	15.6	388.2	4.1
pH 5	11.6	139.6	5.3	27.3	682.0	5.3
pH 7	11.9	142.9	6.1	27.8	692.9	6.1

D = Intermittent leaching (resins).

E = Perfusion (resins).

F(1) = Shaken under air (soil).

F(2) = Shaken under nitrogen (soil).

TABLE 3
Iron uptake of untreated and of methylated O.M.

Fe Uptake	Untreated O.M.	Methylated O.M.	
		I	II
mg. Fe/g. O.M.			
pH 3	16.39	11.55	0.06
pH 5	22.37	10.88	1.96
mmoles Fe/mole O.M.			
pH 3	196.92	146.82	0.84
pH 5	268.84	128.33	27.44

within limits, of aluminum taken up from the soil [procedures *F(1)* and *F(2)*]. The amounts of both metals mobilized were considerably higher at pH 5 and 7 than at pH 3. It made little difference whether the suspensions were originally adjusted to pH 5 or 7. The final pH of the suspensions originally adjusted to pH 3 and 5 increased, whereas the pH of those adjusted to 7 decreased.

The data in table 3 clearly show that, as more and more of the acidic groups were blocked, the amounts of iron taken up decreased. The iron uptake of methylated O.M.-II at pH 3 was practically zero. The small uptake at pH 5 might be ascribed to partial hydrolysis of the methylated product at this pH.

DISCUSSION

The data in tables 1 and 2 clearly indicate that this type of O.M. has a remarkable capacity of forming stable complexes with inorganic soil constituents. The highest complexes formed in the uptake experiments were 1:1 molar in agreement with findings published in the earlier report (9) for water-soluble complexes between O.M. and iron and aluminum. While, in the experiments described in that report, in addition to 1:1 molar complexes 2:1 molar complexes were also formed between iron and O.M. at pH 5, the formation of 2:1 complexes was not detected in the uptake experiments. It is noteworthy that in the present investigation 1:1 molar complexes were formed under the most favorable conditions (in the perfusion apparatus) only. In this instance continuous wetting and leaching were provided for, indicating that conditions of contact between metal and O.M. are very significant. In most experiments the molar ratios were considerably lower.

A point of interest in the rise in pH of the metal-enriched solutions after contact with goethite and gibbsite, which occurred at all pH values except in one case (perfusion of goethite with O.M. at pH 5). This can be rationalized on the basis of neutralization of a carboxyl group. It was shown earlier (9) that there was considerable variation in the acid strength of the six carboxyl groups of the O.M. If the most acid carboxyl group reacted with one atom of iron or aluminum, the reactions might be represented by the following equations:



and



Where R denotes the O.M. molecule without the six carboxyl groups. The result would be a decrease in acidity and a rise in pH.

The pH of the suspensions after contact with the soil increased when the original pH was 3 and 5, and decreased when it was 7. In this case the buffering capacity of the soil probably had more effect than reactions such as those illustrated above. With soil as the source of metals, iron and aluminum were present simultaneously. The sum of the moles of iron plus aluminum, taken up by 1 mole of O.M., was as high as 0.84 [table 2, procedures $F(1)$ and $F(2)$], which approaches a metal-O.M. ratio of 1:1.

One g. of soil contained 13.15 mg. of total iron and 6.37 mg. of "free" iron [by the method of Mackenzie (3)]. Similarly, 44.00 mg. of total and 5.66 mg. of easily soluble aluminum (as extracted under conditions of Mackenzie's method) were present in 1 g. of soil.

From the data in table 2 [procedures $F(1)$ and $F(2)$ at pH 5 and 7] one can calculate that 95 mg. of O.M. extracted 1.13 mg. of iron, corresponding to approximately 9 per cent of the total and 18 per cent of the "free iron." Under the same conditions 2.64 mg. of aluminum was extracted. This represented approximately 6 per cent of the total and 47 per cent of the easily soluble aluminum. On the basis of these data, 1 g. of O.M. would extract all of the iron and 63 per cent of the aluminum in 1 g. of this soil. This illustrates the extracting power of this type of O.M. for iron and aluminum from soils.

It has been suggested that diazomethane methylates carboxyl groups in preference to phenolic hydroxyls (4). The experimental results reported herein appear to support this view for the following reasons: (a) each molecular weight of O.M. contains six COOH and two phenolic OH groups, adding up to a total effective acidity of eight active hydrogens; (b) two consecutive methylations resulted in the methylation of six of these groups; and (c) the iron uptake of this methylated product was practically reduced to zero.

Although these results do not exclude possible methylation of phenolic OH groups, they certainly prove, in agreement with preceding experiments, that COOH groups play a most important role in the organo-metallic reactions.

Further work on the chemical structure of the O.M. is needed before the part played by phenolic OH groups in these reactions can be properly understood.

SUMMARY

The uptake by O.M. of iron and aluminum from hydrous oxides and metal-enriched exchange resins, and from a soil material under a variety of conditions such as might be encountered in podzol profiles, was investigated.

On continuous wetting and leaching in a perfusion apparatus, in 1 week 1.0 mole of O.M. mobilized 1.0 mole of iron from goethite and an iron-saturated exchange resin, and 1.1 mole of aluminum from aluminum-saturated exchange resin. Metal uptake on standing and shaking, and on intermittent leaching, was considerably lower.

The effect of pH was difficult to estimate. In the perfusion experiments it had no effect. In reactions with goethite and gibbsite, metal uptake decreased with increase in pH, whereas the opposite was essentially true when O.M. reacted with soil material.

Atmosphere (air *vs.* nitrogen) had no apparent effect on iron uptake by O.M.

Methylation of most of the active acid groups reduced iron uptake to very low values, thus demonstrating the important role of carboxyl groups in the organo-metallic reactions.

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